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DYNAMICS AND CONVERGENCE ACCELERATIONS OF RAPID PRESSURE SWING ADSORPTION

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By

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DYNAMICS AND CONVERGENCE ACCELERATIONS OF RAPID PRESSURE SWING ADSORPTION

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May 2005

Supervisor : Thomas Choong Shean Yaw, PhD

Faculty : Engineering

Rapid Pressure Swing Adsorption (RPSA), a type of Pressure Swing Adsorption (PSA) process, offers promising solution to size and portability issues for the development of fuel cell powered vehicles and medical-grade oxygen concentrator. In this dissertation, numerical simulations of RPSA models are carried out using the Instantaneous Local Equilibrium (ILE) and Linear Driving Force (LDF) as the mass transfer models. A physically consistent RPSA model identified by Choong *et al.* (1998) is adopted for the numerical simulation of RPSA process. The verification of the applied numerical method and computer programs has been carried out successfully.

The numerical simulation of RPSA models requires a sufficiently large number of cycles to reach cyclic steady state (CSS), resulting in large computational time. Hence, convergence acceleration methods are examined. The methods are extended from the accelerated successive substitution method of Choong (2000). The problem where the Aitken-like extrapolator (first extrapolator) and the MSS approach the CSS from the same side, with condition $k^{(n)} > k^{(n-1)}$, which was not solved by Choong (2000), is investigated in this work. The Secant-like extrapolator (second

extrapolator) provides a satisfactory extrapolator for reaching CSS from the opposite side of the first extrapolator. Further, the Muller method is found to reach CSS faster than the Secant-like extrapolator by approximately 250%.

The numerical simulation of URPSA models is challenging because small time steps are required to capture the process dynamics of cycle time within fractions of seconds. Studies are carried out to assess the suitability of LDF model to describe the mass transfer mechanism for URPSA process by: (1) considering the effect of external fluid film resistance provided by Choong and Scott (1998); (2) comparing the LDF model with a full diffusion model provided by Todd and Webley (2002). The LDF model is considered sufficient to describe the mass transfer mechanism in the particle for the numerical simulation of URPSA considered in this work. The effects of axial dispersion and feed pressure boundary conditions on the performance of URPSA are studied. Increasing the value of effective axial dispersion reduces substantially the oxygen product purity. However, the axial dispersion has no effect on the cycle-averaged feed gas rate. The simulated cycle-averaged feed gas rate using the step function as the feed pressure boundary condition overestimates the experimental cycle-averaged feed gas rate by 100%. However, this is a substantial improvement over the 600% overestimation by Murray (1996). Using the exponential function as the feed pressure boundary condition provides a better prediction of the experimental cycle-averaged feed gas rate than that of the step function. Nevertheless, the forms of feed pressure boundary condition have no effect on the oxygen product purity.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

DINAMIK DAN PENCEPATAN PERTEMUAN UNTUK PENYERAPAN PANTAS BUAIAN TEKANAN

Oleh

SOO CHING YEE

Mei 2005

Penyelia **: Thomas Choong Shean Yaw, PhD**

Fakulti **: Kejuruteraan**

Penyerapan pantas buainan tekanan (RPSA), adalah salah satu jenis proses penyerapan buainan tekanan (PSA), menawarkan cara penyelesaian kepada masalah saiz dan pengangkutan untuk perkembangan kenderaan yang menggunakan sell bahan api dan pemekat oksigen pangkat perubatan. Dalam tesis ini, simulasi pembilangan untuk model RPSA dijalankan dengan menggunakan model-model pemidahan jisim yang bernama keseimbangan setempat segera (ILE) dan angkatan pemandu lurus (LDF). Satu RPSA model mengikuti kenyataan tetap RPSA yang dikembangkan oleh Choong *et al.* (1998) telah digunakan untuk simulasi pembilangan proses RPSA.

Simulasi pembilangan model RPSA memerlukan banyak pusingan untuk mencapai pusingan kedudukan stabil (CSS), dan ini menyebabkan masa komputer yang panjang. Oleh sedemikian, cara pencepatan pertemuan dikajikan dalam penyelidikan ini. Cara dikajikan adalah sambungan daripada kerja oleh Choong (2000) dalam cara pencepatan penggantian berikut. Masalah yang tidak ditimbangkan oleh Choong (2000), iaitu peramal seperti-Aitken (peramal pertama) dan MSS mencapai CSS dari arahan yang sama dengan syarat $k^{(n)} > k^{(n-1)}$, telah dikajikan dalam penyelidikan ini.

Peramal seperti-Secant (peramal kedua) menjadi peramal yang memuaskan untuk mencapai CSS dari arahan yang bertentangan dengan arahan peramal pertama, tetapi, cara Muller didapati mencapai CSS 250% lebih cepat daripada peramal kedua.

Simulasi pembilangan model-model URPSA adalah mencabarkan kerana langkah masa yang kecil diperlukan untuk menghuraikan proses dinamik jangka masa sependek pecahan saat. Pengajian untuk menilai kelayakan model LDF dijadikan model pemidahan jisim dalam proses URPSA dijalankan dengan: (1) menimbangkan kesan rintangan cecair filem luar yang dibagikan oleh Choong dan Scott (1998); (2) membandingkan model LDF dengan model yang mempunyai penyibaran penuh yang dibagikan oleh Todd dan Webley (2002). Model LDF didapati menghuraikan pemindahan jisim dalam zarah adalah mencukupi untuk simulasi pembilangan URPSA. Kesan pembuburan paksi dan keadaan tekanan penyuap telah dikajikan. Dengan meningkatkan angka pembuburan paksi berkesan, ketulinan produk oksigen akan diturunkan, tetapi kadar pusingan purata gas penyuap tidak berubah. Kadar pusingan purata gas penyuap yang disimulasikan dengan menggunakan fungsi langkah sebagai keadaan tekanan penyuap didapati melebihi 100% daripada kadar pusingan purata gas penyuap eksperimen. Ini menunjukkan perkembangan yang banyak berbanding dengan hasil simulasi Murray (1996) yang melebihi 600% kadar pusingan purata gas penyuap eksperimen. Dengan menggunakan fungsi exponent sebagai keadaan tekanan penyuap dapat menghasilkan kadar pusingan purata gas penyuap simulasi yang lebih dekat dengan kadar eksperimen. Namun sedemikian, perubahan keadaan tekanan penyuap tidak ada kesan ke atas ketulinan produk oksigen.

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I certify that an Examination Committee met on 14th May 2005 to conduct the final examination of Soo Ching Yee on her Master of Science thesis entitled "Dynamics and Convergence Accelerations of Rapid Pressure Swing Adsorption" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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Date: 1 1 AUG 2005

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

Ching Yee Soo.
SOO CHING YEE

Date: 18 JULY 2005

LIST OF NOTATIONS

A	bed cross sectional area	m^2
$A_{j,m}$	first derivative of the Lagrange interpolation polynomial	
$B_{j,m}$	second derivative of the Lagrange interpolation polynomial	
Bi_m	Biot number for mass transfer	
c	gas phase concentration	mol m^{-3}
c^p	gas phase concentration in the pore	mol m^{-3}
$d_{molecule}$	diameter of a spherical molecule	m
d_c	bed diameter	m
d_p	particle diameter	m
d_{pore}	macropore diameter	m
D	effective axial dispersion coefficient	$m^2\ s^{-1}$
D_{ax}	axial dispersion coefficient	$m^2\ s^{-1}$
D_c	micropore diffusion coefficient	$m^2\ s^{-1}$
D_e	effective diffusion coefficient	$m^2\ s^{-1}$
D_e^*	modified effective diffusion coefficient	$m^2\ s^{-1}$
D_f	diffusion coefficient across the external fluid film	$m^2\ s^{-1}$
D_k	Knudsen diffusion coefficient	$m^2\ s^{-1}$
D_m	molecular diffusion coefficient	$m^2\ s^{-1}$
D_p	pore diffusion coefficient	$m^2\ s^{-1}$
Err	relative material balance error	%
H	Henry's law constant	$m^3\ kg^{-1}$
h_k	width of element k	
i	an index	
j	an index	

J	order of polynomial in the method of OC	
J_v	bed permeability	N s m^{-4}
J_k	coefficient in the Ergun equation	N s^2 m^{-5}
k_{LDF}	LDF mass transfer coefficient	s^{-1}
K_{LDF}	dimensionless LDF mass transfer coefficient	
k	slope of the semilog plot of advance *vs.* n	
k'	slope of P *vs.* η	bar
k_f	external fluid film mass transfer coefficient	s^{-1}
ℓ_m	a Lagrange interpolation polynomial	
L	length of bed	m
m	an index	
$\hat{M}$	cumulative molar amount at any time during a step	
$\overline{M}$	dimensionless cumulative molar amount	
M	pressurisation or blowdown step rate	s^{-1}
M_w	molecular weight	
N	number of space discretisation points	
n	number of cycles or number of iterations	
$\tilde{n}^{(\infty)}$	predicted number of cycles required to reach CSS	
$\hat{n}^{(\infty)}$	cycles at which CSS predicted to be reached	
P	total bed pressure	Pa or bar
Pe_∞	limiting value of the Peclet number	
$PROD$	adsorbent productivity	mol kg^{-1} s^{-1}
q	adsorbed phase concentration	mol kg^{-1}
q^*	equilibrium adsorbed phase concentration	mol kg^{-1}
$\overline{q}$	adsorbed phase concentration averaged over an entire particle volume	mol kg^{-1}
$\overline{Q}_f$	cycle-averaged feed gas rate	m^3 s^{-1}
$\overline{Q}_p$	product delivery rate	m^3 s^{-1}
r	radial co-ordinate of a particle	m

r_p	radius of an adsorbent particle	m
R	uptake rate by the particles per unit volume of the bed	mol m^{-3} s^{-1}
Re_p	particle Reynolds number	
REC	oxygen product recovery	
S	dependent variable	
Sc	Schmidt number	
Sh	Sherwood number	
u	superficial gas velocity	m s^{-1}
$\bar{u}$	dimensionless superficial gas velocity	
t	time	s
t_f	duration of pressurisation	s
t_w	duration of depressurisation	s
t'	any time measured from the start of a step	s
t_c	cycle time	s
t_c^*	cycle half time	s
t_m	characteristic time constant for macropore diffusion	s
t_{cr}	characteristic time constant for micropore diffusion	s
T	temperature	K or ° C
X	dimensionless number as defined in section 4.2.1	
x	variable in section 4.3	
$\Delta x^{(\infty)}$	as defined by equation (4.3.3)	
$\hat{x}^{(n)}$	value obtained by extrapolation from iteration number *n* using the first extrapolator	
$\hat{\hat{x}}^{(n)}$	value obtained by extrapolation from iteration number *n* using the second extrapolator	
$\hat{\hat{x}}_m^{(n)}$	value obtained by extrapolation from iteration number *n* using the Muller method	

y	gas phase mole fraction	
y_p	oxygen product purity averaged over a complete cycle	
Δy_p	advance of oxygen product purity	
z	axial co-ordinate	m

Greek letters

α, β	integers in Jacobi orthogonal polynomials	
α_h	thermal diffusivity	$m^2\ s^{-1}$
β_{ax}	radial dispersion factor	
δ	thickness of the stagnant film surrounding a spherical particle	m
Δ	absolute difference between two values	
ε_b	bed porosity	
ε_p	particle porosity	
ε_t	total bed porosity	
ϕ	dimensionless bed pressure	
η	similarity variable	
φ	dimensionless adsorbed phase concentration	
$\bar{\varphi}$	dimensionless adsorbed phase concentration averaged over an entire particle volume	
φ^*	dimensionless equilibrium adsorbed phase concentration	
μ	gas viscosity	$N\ s\ m^{-2}$
θ	dimensionless time	
θ_c	dimensionless cycle half time	
ρ_b	bed bulk density	$kg\ m^{-3}$
ρ_g	gas density	$kg\ m^{-3}$
τ	dimensionless time	
τ_{ax}	axial tortuosity factor	

τ_p	pore tortuosity factor
Ω	dimensionless function
ξ	dimensionless axial co-ordinate
$\hat{\xi}$	normalised dimensionless axial co-ordinate

Subscripts

am	ambient conditions
accum	accumulation in the bed
f	feed, far upstream of $z = 0$
feed	feed end of the bed
i	component oxygen or nitrogen
init	initial values
product	product end of the bed
p	product end of bed
O_2	oxygen
N_2	nitrogen
w	waste
(min)	minimum

Superscripts

acc	significant figures specified in the oxygen product purity
(n)	n^{th} cycle or n^{th} iteration
(∞)	at CSS

LIST OF ABBREVIATIONS

ADPF	axially dispersed plug flow
ADSIM	ADsorption SIMulator (commercial software package from AspenTech (1997))
BC	boundary condition
BzzOde	ODE solver developed by Dr. G. Buzzi Ferraris and Dr. D. Manca
BDF	backward differentiation formulae
CIS	Cells-in-series
CPU	computer processing unit
CSS	cyclic steady state
DPM	Discretised Pellet Model
E	experiment
FPM	full pellet model
gPROMS	general PROcess Modelling System
I	intensified RPSA
ILE.	instantaneous local equilibrium
LDF	linear driving force
M	modelling
MMS	Mass-transfer Model Switch
MSS	method of successive substitution
OC	orthogonal collocation
OCFE	orthogonal collocation finite elements
ODE	ordinary differential equation
PDE	partial differential equation
PSA	pressure swing adsorption
RPSA	rapid pressure swing adsorption
TOL	tolerance used in the ODE solver
URPSA	ultra rapid pressure swing adsorption
VF+DGM	Viscous Flow plus Dusty Gas Model
VODE	Variable coefficient Ordinary Differential Equation Solver

CHAPTER 1

Introduction

1.1 Background

Rapid pressure swing adsorption (RPSA), a type of pressure swing adsorption (PSA) processes, which employs a single bed has gained some attention recently due to its process simplicity and relatively higher adsorbent productivity (Yuwen *et al.*, 2004; Ackley *et al.*, 2003; Keefer *et al.*, 2003; Todd *et al.*, 2003; Todd and Webley, 2003; Choong *et al.*, 2002; Ding and LeVan, 2001; Ko and Moon, 2000; Andrews and Scott, 1999; Kulish *et al.*, 1998). RPSA provides promising solution to size and portability issues, *e.g.* for the development of fuel cell powered vehicles and medical-grade oxygen concentrator. Numerical simulation offers an economical means for parametric studies for being a prelude to pilot plant studies. The numerical simulation of RPSA models requires a large number of cycles to reach cycle steady state (CSS), resulting in large computational time. Therefore, methods that reduce the computational time are desirable. Recent development of RPSA focuses on process intensification, *i.e.* Ultra Rapid Pressure Swing Adsorption (URPSA). The adsorbent productivity can be increased substantially by using shorter adsorbent bed and rapid cycle operation, *e.g.* Murray (1996) used 0.2 m bed with cycle times ranging from 0.2 s to 2 s. The numerical simulation of URPSA models is challenging because small step changes are required to capture the dynamics of URPSA which operates within cycle time of fractions of seconds, rather than the commonly found cycle time of 5 s in RPSA processes.

1.2 Difference between RPSA and PSA

RPSA was originally developed by Turnock and Kadlec in early 1970 and commercialized by Jones and Keller in 1980, eliminating the need for multiple adsorbent beds as required in conventional pressure swing adsorption process. RPSA uses the similar principles of a PSA process except for the following apparent differences:

1) RPSA employs only one adsorbent bed.
2) RPSA adsorbent particles are relatively smaller, <700 μm in diameter (Ko and Moon, 2000).
3) RPSA processes operate below a total cycle time of thirty seconds. (Todd, 2003).
4) Axial pressure gradient in the adsorbent bed is crucial for RPSA operation.

Technically, the advantages of a RPSA unit are:

1) smaller adsorbent bed and fewer operating hardwares are required.
2) shorter time cycle.
3) constant product flow is achieved using only one bed.
4) self-purging is sufficient to remove adsorbates from adsorbents during desorption.

However, RPSA is economically feasible only for small scale applications because of high operating cost (Choong, 2000).

1.3 Principle of Rapid Pressure Swing Adsorption

Referring to Figure 1.3.1 (p.8), a basic RPSA cycle consists of two steps: pressurisation and depressurisation. During pressurisation, the feed point of the three-way valve is opened to allow the air to be fed into the adsorbent bed. Pressure is increased rapidly at the entry of the bed. As feed air flows through the column, nitrogen is selectively adsorbed on the zeolite 5A adsorbent, resulting in an oxygen-enriched product gas flow.

In the depressurisation step, the feed point of the three-way valve is closed and the exhaust port of the three-way valve is opened to atmospheric pressure, a rapid pressure drop at the feed end of the column will occur. Such rapid pressure drop results in the desorption of nitrogen from the adsorbent bed. At this stage, a pressure gradient is always maintained between this maximum and the product end of the bed which ensures that a continuous product stream throughout the cycle. In order to guarantee constant product flowrates, a surge tank is installed as a buffer tank (Jones and Keller, 1981). Sometimes a delay step is incorporated between the pressurisation and depressurisation steps to allow the pressure wave to penetrate further into the bed (Jones and Keller, 1981; Pritchard and Simpson, 1986).

In a complete cycle (*i.e.* pressurisation and depressurisation), pressure variations are common in the feed end of the bed. The product end pressure remains constant with time because of pressure gradient on the lower half of the bed being maintained even during depressurisation (refer Figure 1.3.2, p.9). In contrast to the PSA process, flow resistance in the bed, often described by the Ergun equation, plays an important role for a RPSA process to be successful (Choong, 2000). This resistance can be manipulated by using different adsorbent particle size.

For the focus of this study, a cycle is initiated at the start of pressurisation and completes at the moment of the end of depressurisation step. No delay step is included in this study. The effect of the dead volumes in the upstream and downstream of the adsorbent bed is considered negligible here.

1.4 Numerical Simulation for Modelling Dynamics of RPSA processes

The nature of RPSA process has no steady state like general continuous process, but it has a cyclic steady state (CSS) (Suzuki, 1990). When the operation of RPSA process is initiated, the process undergoes a transient stage prior to reach a cyclic steady state (CSS). The method of successive substitution (MSS) is the traditional way of simulating RPSA process to reach CSS. MSS describes the dynamics of the process by calculating the values for the new cycle based on the previous cycle. Depending on the problem and initial conditions, MSS may require hundreds or thousands of cycles to achieve CSS (Choong, 2000). It is very undesirable because it may take up to several weeks or months (depending on the kind of problem and initial conditions are used) to complete the computation of CSS. For design problems, the CSS is of importance. Therefore, the study of convergence acceleration methods is important for reducing the computing time. There are two classes of methods to accelerate the simulation of RPSA models, namely, accelerated successive substitution method and direct determination method. The class of accelerated successive substitution method is examined in this work because of its ease for implementation compared to that of direct determination method.

The numerical simulation of URPSA model is challenging because small time steps are required to capture the dynamics of URPSA which operates within cycle time of fractions of seconds. Earlier simulations of URPSA process carried out by Murray (1996) using general PROcess Modelling System (gPROMS) were not successful. His simulated cycle-averaged gas feed rate overestimated the experimental value by up to 600%. This study aims to improve the numerical simulation of the URPSA process.

1.5 Objectives of this Study

The previous sections of this chapter have highlighted on the background and importance of this study. The overall objective can be summarized as follows:

1. to develop computer programs using physically consistent RPSA models for the Instantaneous (ILE) and Linear Driving Force (LDF) models.
2. to carry out verification of the applied numerical methods and developed computer programs.

3. to extend the work of Choong (2000) on the convergence acceleration methods for cyclic processes.
4. to study the effects of axial dispersion and feed boundary conditions on the numerical simulation of URPSA using Murray's (1996) experimental conditions.

The objectives are achieved and presented over three chapters. Chapter 2 presents a brief survey on the published RPSA literature. This chapter also discusses some advances in modelling and numerical simulation of RPSA based on the model formulation suggested by Choong *et al.* (1998). Computer programs written in FORTRAN 90 were developed for the simulation. The aspect of convergence acceleration of CSS will also be highlighted in this chapter. Chapter 3 presents two models of RPSA. Chapter 4 consists of three sections. The first section verifies the discretisation method used in this study and the three important process parameters, which are the oxygen mole fraction, total bed pressure and cycle average flow rates are then verified. The second section presents the work done for the reduction of computing time. This part begins with a brief description of the methods of accelerated successive substitution developed by Choong (2000). The work of Choong (2000) is then extended in this work. The last section of Chapter 4 presents the simulation of URPSA. This section includes the assessment of the suitability of the LDF model to resemble the dynamics of URPSA process and the effects of two process conditions (axial dispersion and feed pressure boundary conditions) on the prediction of the experimental results.

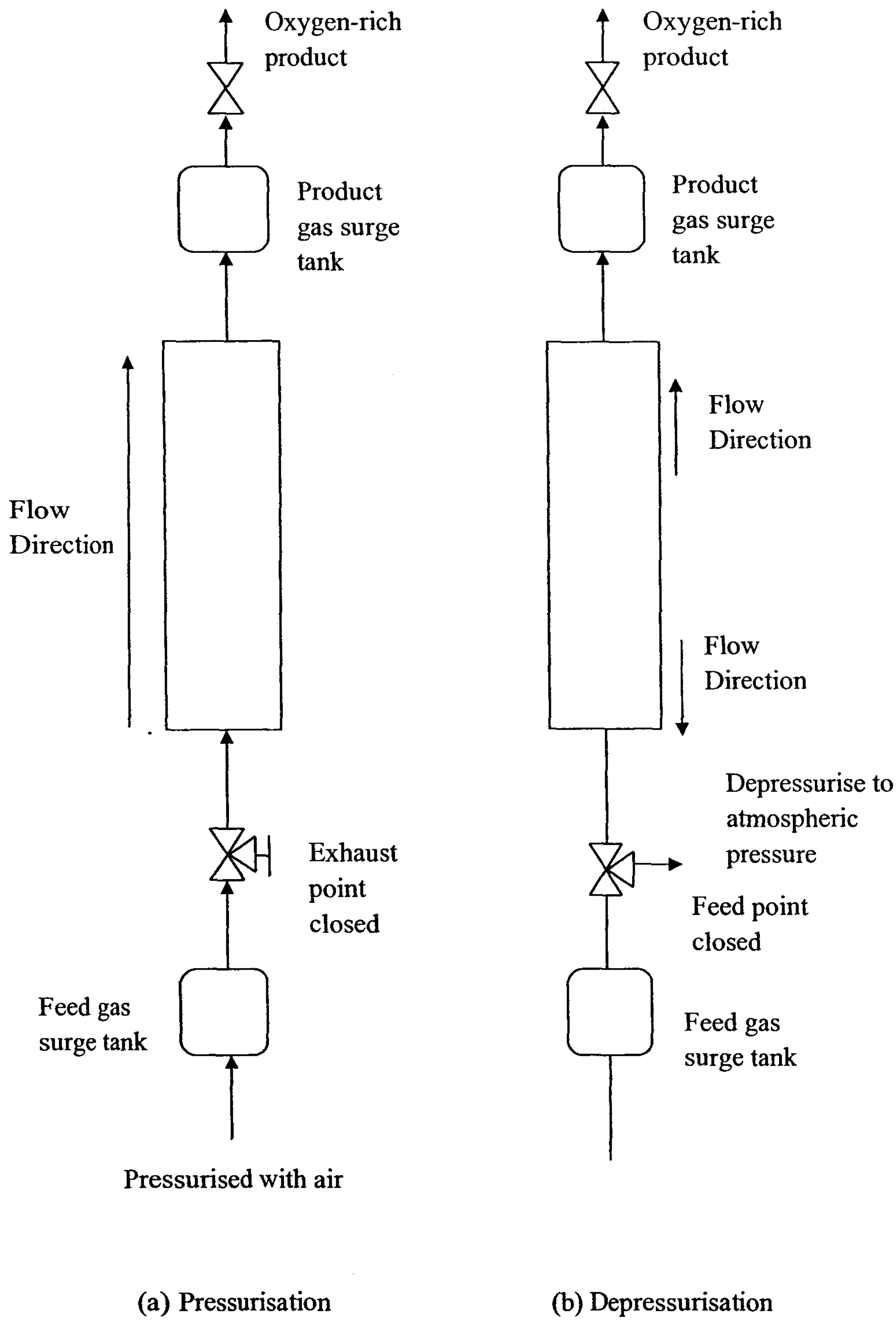

Figure 1.3.1 Basic steps in RPSA (Choong, 2000).

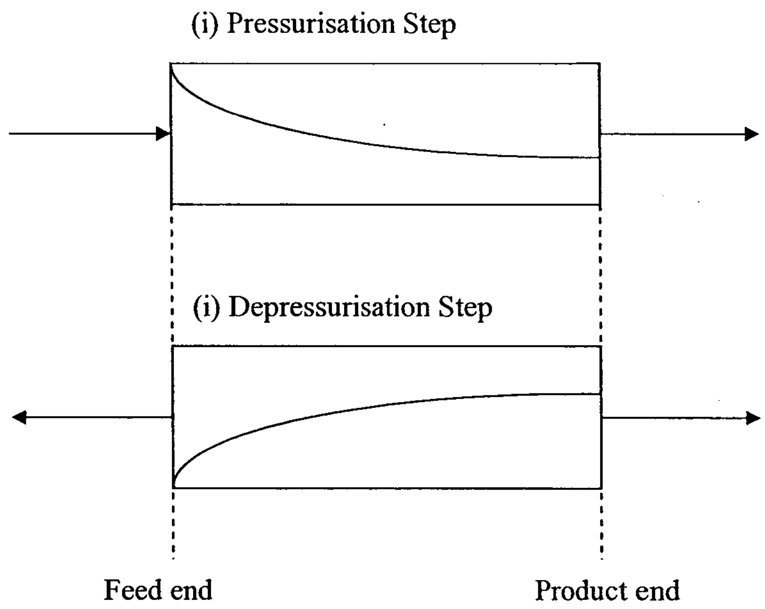

Figure 1.3.2 Pressure Profile of the Pressurisation and Depressurisation Steps in an Adsorbent Bed (Todd, 2003).